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Reduced-dimensionality study of the reaction of methane with H atom

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Abstract

The $CH_4 + H \rightarrow CH_3 + H_2$ reaction is a major chain-propagation reaction in the combustion of natural gas. The accurate quantum mechanical description of its dynamics cannot be performed; only reduced-dimensional models can be applied. The goodness of the reduced-dimensionality model cannot be predicted *a priori*, however, it can be assessed using classical mechanical modeling. We studied a reduced-dimensional model in which the CH_3 group is constrained to C_{3v} symmetry. Both full- and reduced-dimensional quasiclassical trajectory calculations for the reactive collisions between $CD_4 + H$ and $CD_3H + H$ were performed, and their results were compared with each other. The classical mechanical reaction cross sections obtained with the reduced-dimensionality method agree well with the full-dimensional ones for the $CD_3H + H$ isotope combination but not for the $CD_4 + H$ reaction. The details of applicability and its consequences are discussed in the paper.

Introduction

Methane is the main component of natural gas. One of the most important ways of its utilization is energy production by combustion. The

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad (R1)$$

reaction is one of the main propagation reactions in the combustion of natural gas, and is the prototype of hydrogen-abstraction reactions from hydrocarbons and other similar five-atomic reactions. Because of its significance, its kinetics and dynamics are primary targets of detailed studies. The dynamics of the $CH_4 + H$ reaction itself is not easy to study experimentally, whereas there are numerous experimental data available on isotopologues [1–6] such as

$$CD_4 + H \rightarrow CD_3 + HD \qquad (R1D)$$

and

$$CD_3H + H \rightarrow CH_3 + H_2. \qquad (R1H)$$

Theories of elementary gas-phase reactions allow one to rationalize the experimental data. The detailed theoretical description of the dynamics of reaction (R1) would require the use of quantum mechanics. However, for systems involving more than 4 atoms, the full-dimensional quantum mechanical (FDQM) calculations cannot be performed. Several reduced-dimensionality quantum mechanical (RDQM) methods have been worked out in which the degrees of freedom thought to be the most important are treated explicitly, the rest are kept frozen [7,8]. Unfortunately, no one knows what is missed when a reaction is described by using the RDQM methods. Fortunately, however, classical and quasiclassical trajectory calculations (CT, QCT) can be performed both in full and in reduced dimensionality. One can develop the classical analogue of each RDQM method, and the comparison of the results of full- and reduced-dimensional classical calculations allows us to assess the qualitative features that are and those that are not correctly described by the given RDQM.

We implemented the classical version of a reduced-dimensional model [8,9] of $CZ_3Y + X$ type reactions. The only restriction in this model is that the CZ_3 group is constrained to C_{3v} symmetry. We performed quasiclassical trajectory calculations with the method, using fitted analytic potential surfaces [10–12].We performed both full- and reduced-dimensional quasiclassical trajectory calculations (FDQCT, RDQCT) on reactions (R1D) and (R1H), and compared their results with each other, to estimate the importance of the dimensionality reduction.

The reduced-dimensional model for $CZ_3Y + X$ type reactions

The CH_5 system has 18 degrees of freedom, of which 6 describe the overall rotation and translation, leaving 12 for internal coordinates. Palma and Clary [9] proposed an 8-dimensional model (from now on referred as Palma-Clary model) to describe reactions of CZ_3-Y+X type by constraining a CZ_3 moiety to C_{3v} symmetry. This implies that all three C-Z bond lengths and Z-C-Z bond angles are constrained to be identical, which can be formulated by four equalities, together reducing the number of internal degrees of freedom to 8.

$$f_1(\mathbf{x}_{3N}) = \mathbf{r}_{CZ1}^2 - \mathbf{r}_{CZ2}^2 = 0 \qquad (1)$$

$$f_2(\mathbf{x}_{3N}) = \mathbf{r}_{CZ2}^2 - \mathbf{r}_{CZ3}^2 = 0 \qquad (2)$$

$$f_3(\mathbf{x}_{3N}) = \mathbf{r}_{CZ1}\mathbf{r}_{CZ2} - \mathbf{r}_{CZ2}\mathbf{r}_{CZ3} = 0 \qquad (3)$$

$$f_4(\mathbf{x}_{3N}) = \mathbf{r}_{CZ2}\mathbf{r}_{CZ3} - \mathbf{r}_{CZ3}\mathbf{r}_{CZ1} = 0 \qquad (4)$$

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Here, $\mathbf{r}_{AB}$ denotes the vector between atoms A and B, and Z^1 and Z^2 and Z^3 are the Z atoms in CZ_3. Regarding CZ_3Y molecule, the constraints reduce its degrees of freedom from 9 to 5, therefore this model will be referred to as 5D model.

In our CH_5 system these constraints make the corresponding three C-H bonds of the CZ_3 group virtually unbreakable as it would require the simultaneous rupture of all of them. Therefore only the fourth H atom (Y) can be abstracted or substituted, thus for direct comparison the cross sections and rates obtained from full-dimensional simulations have to be divided by four in systems where Y and Z represent the same nuclides.

For the preparation of the initial vibrational state of the 5D methane we used the internal coordinates shown in **Error! Reference source not found.** Coordinate l denotes the distance of the vertices of the $Z^1Z^2Z^3$ regular triangle from its center, and s is the distance between atom C and the Z_3 center of mass of $Z^1Z^2Z^3$ atoms. These two coordinates are the same as those used in the Palma-Clary model [9]. In addition, we defined a Cartesian frame fixed to CZ_3 with its origin at C and the position of the fourth H atom (Y) given by 3 Cartesian coordinates (x_Y,y_Y,z_Y) in this frame.

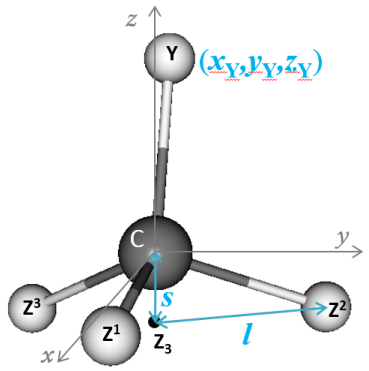

Fig. 1. Internal coordinates of the reduced-dimensional model of methane used for normal mode sampling of initial states. The CZ_3 group is constrained to C_{3v} symmetry.

The simulation of the collisions was carried out using 18 Cartesian coordinates in center-of-mass frame. In the reduced-dimensionality model the constraints (1)-(4) were enforced by calculating the constraint forces using the Lagrange multiplier method [13].

Potential energy surfaces

We used three analytic potential energy surfaces (PES) describing the ground electronic state of the system. The investigated CH_5 PESs were developed by Espinosa-Garcia [10], Corchado et al. [12] and Zhang et al. [11]. These potential surfaces will be referred to as EG-2002, EG-2009 and ZBB3, respectively. These are Born-Oppenheimer PESs therefore they are equally applicable to any CH_4 + H isotope combination. The EG-2002 and EG-2009 surfaces are based on an analytical expression proposed by Jordan and Gilbert [14] and were developed for describing the abstraction reaction only. The functional form used in these PESs is invariant to the permutation of 4 H atoms within CH_4, but not for the attacking fifth H atom. The EG-2002 PES was calibrated with respect to the theoretical and experimental data available at the time it was developed. The EG-2009 PES was obtained by reoptimizing the parameters of EG-2002 PES to reproduce *ab initio* electronic structure calculations obtained at the CCSD(T)/cc-pVTZ level. These PESs also provide analytical derivatives.

The ZBB3 PES is based on an earlier PES function, called ZBB1 [15], which was obtained by fitting a symmetrized polynomial of some exponential functions of the interatomic distances to over 20000 *ab initio* energies obtained at the CCSD(T)/aug-cc-pVTZ level. Further *ab initio* points were calculated in the regions of the two van der Waals minima (pre- and post-reaction) and of the exchange saddle point and the ZBB1 PES was refined to give the ZBB3 PES [11]. The ZBB3 PES is invariant to the permutation of all five H atoms and was developed to describe both abstraction and substitution reactions. From the point of view of trajectory calculations it is a disadvantage that the ZBB3 PES subroutine does not provide analytical derivatives, therefore trajectory evolution with numerical derivatives is 2-3 orders of magnitude slower than in the case of both EG PESs. Earlier tests of the potential surfaces indicated that the EG-2002 PES overestimates the cross sections by about a factor of 4 [3–5,12,16]. The EG-2009 PES was shown to be correct in dynamics calculations up to E_{coll}=1eV [16] with respect to ZBB3. It was also found that the ZBB3 PES performs well in comparison with an even more accurate PES (ZFWCZ) developed in paper [16].

Normal mode analysis

For the preparation of the initial vibrational states of methane molecules we applied normal mode sampling, which is the standard method in quasiclassical trajectory calculations. Normal mode vibrational analysis of the molecules were carried out for both the full- and reduced-dimensionality models of CD_4 and CD_3H on all three potential energy surfaces at the corresponding equilibrium geometries. The normal-mode frequencies are shown in Table 1 (CD_4) and Table 2 (CD_3H).

Except for the doubly degenerate bending vibrational mode of CD_4, the 5D model gives exactly the same frequencies as those found with the FD model. The triply degenerate modes become non-degenerate due to the constraints. The remaining doubly degenerate mode describes the two orthogonal bending vibrations of the D_3-C-D angle.

For the CD_3H isotopogue the original molecule has already C_{3v} symmetry due to the isotopic substitution and the triply degenerate modes split into a doubly degenerate and a non-degenerate mode. In the 5D model of CD_3H, due to the constraints 2 doubly degenerate

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modes disappear. The frequencies of the non-degenerate modes are identical to those in the FD model, while some deviation can be seen in the case of the doubly degenerate modes, which correspond to motion that is a mixture of normal modes in the FD model.

Initial conditions

The normal mode vibrations are uncoupled harmonic vibrations whose energies can be set separately. In quasiclassical trajectory calculations the ensemble of initial conditions of molecules mimics a vibrational quantum state characterized by pre-selected normal mode quantum numbers.

Table 1. Irreducible representation, degeneracy and frequency of normal mode vibrations of CD_4 determined for the FD and 5D models at the equilibrium geometry on three PESs.

Irrep.		Dege-		Frequencies (cm^{-1})					
T_d	C_{3v}	neracy		EG-2002		EG-2009		ZBB3	
FD	5D	FD	5D	FD	5D	FD	5D	FD	5D
T_2	A_1	3	1	1013	1013	1047	1047	1010	1010
E	E	2	2	1062	1106	1097	1143	1095	1122
A_1	A_1	1	1	2042	2042	2118	2118	2141	2141
T_2	A_1	3	1	2260	2260	2344	2344	2344	2344

Table 2. Irreducible representation, degeneracy and frequency of normal mode vibrations of CD_3H determined for the FD and 5D models at the equilibrium geometry on three PESs.

Irrep.		Dege-		Frequencies (cm^{-1})					
C_{3v}	C_{3v}	neracy		EG-2002		EG-2009		ZBB3	
FD	5D	FD	5D	FD	5D	FD	5D	FD	5D
A_1	A_1	1	1	1021	1021	1055	1055	1018	1018
E		2		1036		1070		1046	
E	E	2	2	1282	1337	1325	1381	1306	1355
A_1	A_1	1	1	2090	2090	2168	2168	2187	2187
E		2		2260		2344		2344	
A_1	A_1	1	1	3018	3018	3130	3130	3137	3137

The amplitudes of the normal mode vibrations are set to that corresponding to a classical harmonic oscillator having the energy of the selected quantum state. An ensemble of ground-state methane molecules, corresponding to all zero quantum numbers, were generated by Monte Carlo sampling of the vibrational phases of normal mode oscillators.

The methane molecules were randomly oriented and their angular momentum was set to zero. Collision energies were investigated between 15-80mE_h which covers the range of previous measurements and calculations [1–6]. The initial distance of reactants was set to be $12a_0$, which makes their initial interaction energy negligible ($\leq$0.1mE_h) compared to the vibrational zero-point energy of methane (~40mE_h) and the collision energies. Impact parameters were sampled from zero to $4.5a_0$ according to various ways: at discrete values distributed equidistantly; from a uniform distribution and with weighting proportional to the impact parameter ($\rho(b)= 2b/b_{max}^2$).

Trajectory calculations

Starting from independent initial conditions at least 10^5 trajectories were simulated for both isotopologues and models (FD/5D) in order to observe a statistically significant number (~100-1000) of reactive events. Hamiltonian equations of motion were solved with a Runge-Kutta solver which guaranteed energy conservation within 0.1mE_h.

Most of the trajectories lead to non-reactive scattering and abstraction was the main reactive event, whereas substitution was observed only at large collision energies for a negligible number of trajectories (<5 in 10^5).

Integrated cross sections (ICS or total cross section σ_{tot}), differential cross sections (DCS or $d\sigma/d\Omega$) and reaction probabilities (P) were calculated for the abstraction reaction between CD_4 + H and CD_3H + H both with the FD and RD models on all the three PESs. In the corresponding excitation function ($\sigma_{tot}(E_{coll})$), opacity function ($P(b)$), and angular distribution graphs ($d\sigma/d\Omega(\cos\Theta)$) the data points are connected with straight lines to guide the eye and ±2σ Monte Carlo error bars are shown to assess the agreement between the results of the two models statistically. For the CD_4 + H isotope combination the results of the FD model were divided by 4 to make them directly comparable to the RD results.

Results and discussion

Excitation functions on the three potential energy surfaces

The excitation functions are shown in Fig. 2 and **Error! Reference source not found.** for reactions (R1D) and (R1H), respectively. The threshold energies for all the excitation functions (2 reactions, 2 models, 3 PESs) are around 15mE_h or slightly less. This is significantly smaller than the classical barrier heights (EG-2002: 12.9kcal/mol= 20.6mE_h; EG-2009: 15.1kcal/mol=24.1mE_h; ZBB3: 14.8kcal/mol =23.6mE_h) [12], which suggests there is a significant vibrational zero-point energy (ZPE) leakage. Filtering the trajectories based on whether the internal energy of the products exceeds their ZPE or not is an *ad hoc* way of correcting this problem in QCT simulations. However, this procedure treats the products in the FD and RD models differently, so we prefer making the comparison in their pristine form, i.e. no trajectories lacking product ZPE were discarded.

The ICS values for the EG-2002 PES significantly (~four times) larger than those obtained with the other two PESs. It is obvious that the shape of the excitation functions on EG-2002 and ZBB3 differ significantly, those on EG-2009 fall between the two. The shape of the EG-2002 and EG-2009 excitation functions characteristically differ from those on ZBB3 for reaction (R1H): the former increase monotonously and reach a plateau, the latter passes a maximum. This difference is smaller for reaction (R1D) for which all excitation functions pass a maximum. The more realistic EG-2009 and

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ZBB3 PESs predict similar excitation functions for both reactions at collision energies up to around 30mE_h but the ZBB3 cross sections are higher (beyond statistical error limits) for (R1D). In the high-energy range above 50mE_h, the ZBB3 cross sections are smaller than those on EG-2009. This holds for both the RD and FD model. The observation that the EG-2009 cross sections exceed those on ZBB3 at energies beyond the initial increase is in accord with those of Zhou et al. [16], who found good agreement between the EG-2009 and ZBB3 cross sections for the reaction $CH_4 + H \rightarrow CH_3 + H_2$ below about 40mE_h and differences similar to what we can see for reaction (R1H).

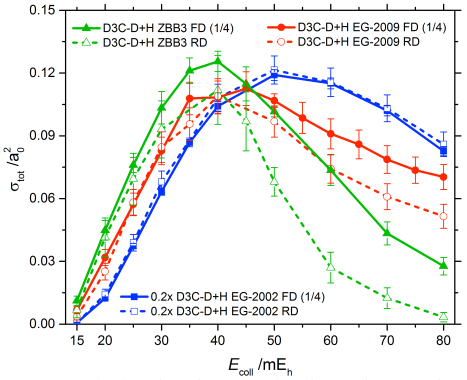

Fig. 2. Excitation functions for the abstraction reaction CD_4+H→CD_3+HD obtained from QCT calculations using the FD and RD models on PESs EG-2002, EG-2009 and ZBB3. The EG-2002 results are scaled down by a factor of 5.

Comparison the reduced- and full-dimensional cross sections

The excitation functions for the FD and RD models agree well for reaction (R1H) on all the investigated PESs.

On the other hand, large differences are observed for reaction (R1D) that depend on the type of the potential surface. The FD and RD cross sections obtained on the EG-2002 PES are essentially identical in the entire studied energy range (after dividing the FD ones by 4). On the EG-2009 and ZBB3 PESs deviations can be observed between them for E_{coll} values above 30 mE_h, which becomes more pronounced with increasing collision energy. The scaled FD cross sections are larger than the RD ones and drop slower with increasing collision energy. The shape of the FD and RD excitation functions for the CD_4+H→CD_3+HD reaction is not similar in the 40-80mE_h range for either of the two more accurate potential surfaces, which means that FD-RD deviation cannot be compensated, not even roughly, by a uniform scaling factor. This differs from what we saw for the other isotopologue (R1H), for which the RD and FD cross sections almost quantitatively agree on all three potential energy surfaces.

It is reasonable to assume that the fictitious FDQM model would accurately describe the reaction, i.e. the FDQM excitation function should overlap with that from the experiment. The comparison of the RD cross sections with the experiment may help one to assess the applicability of the reduced-dimensionality calculations. Zhang *et al.* [6] calculated the RDQM cross sections of the CD_4 + H→ CD_3 + HD reaction with the Palma-Clary model on the ZBB3 PES. The data from their relative cross section measurements were scaled to match the RDQM result at a selected collision energy (61 mE_h). The RDQM calculations describe the abstraction of a single D atom, whereas in the measurement the total abstraction ICS is measured for CD_4. Zhang *et al.* found very good overlap with their own measurement and acceptable agreement with the experimental results (matched at 75.7mE_h) of Camden et al. [3,4,6]: although in the latter case systematic differences were observed, the RDQM results were within the error bars of the experimental ones for collision energies between 55-90mE_h. Assuming that the experimental $\sigma_{tot}(E_{coll})$ function coincides with the FDQM one, the similarity of the shapes of the RDQM and experimental excitation functions suggests that the RDQM cross sections are approximately proportional to the FDQM ones. This has to be compared with our observation that the agreement between the classical RD and FD excitation functions depends on the isotope combination, and for the (R1D) reaction the FDQCT and RDQCT excitation functions are not similar.

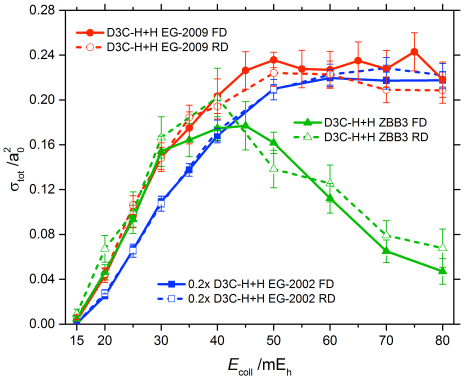

Fig. 3. Excitation functions for the abstraction reaction CD_3H+H→CD_3+H_2 obtained from QCT calculations using the FD and RD models on PESs EG-2002, EG-2009 and ZBB3. The EG-2002 results are scaled down by a factor of 5.

Opacity functions and angular distributions

In order to get more information on which features of the dynamics are involved in the RD vs. FD difference, we calculated the properties characterizing the dynamics in more detail: opacity functions and angular distributions. Since the discrepancies between the results of RDQCT and FDQCT calculations become very significant for the CD_4+H→CD_3+HD reaction above

$50mE_h$ collision energy, we made the comparison at this energy.

The opacity functions of the abstraction and the angular distributions of the scattered HD and H_2 products calculated at $50mE_h$ collision energy were found to agree very well for both isotopologues on the EG-2002 and EG-2009 potential energy surfaces, which is consistent with the good agreement of total cross sections at this collision energy. As expected, remarkable differences can be seen, however, on the ZBB3 PES (that is the most accurate) as can be seen in Fig. 4 and Fig. 5.

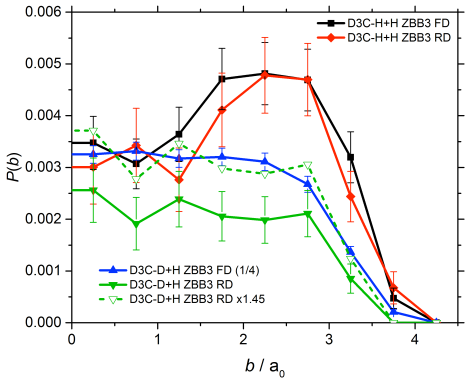

Fig. 4. Opacity functions for the abstraction reactions (R1D) and (R1H) obtained from QCT calculations using the FD and RD models on the ZBB3 PES.

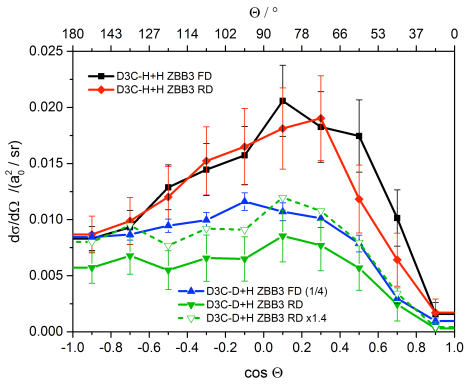

Fig. 5. Angular distributions of the HD/H_2 products for the abstraction reactions (R1D/R1H) obtained from QCT calculations using the FD and RD models on the ZBB3 PES.

While good agreement can be observed between the RD and FD models for reaction $CD_3H + H \rightarrow CD_3 + H_2$ the RD opacity function is uniformly scaled up with respect to the FD curve for the $CD_4 + H$ isotopologue (the shape remains very similar; see the open green triangles in Fig. 4 showing the RD reaction probabilities multiplied by a factor of 1.45). The same holds for the product angular distributions: for reaction $CD_4 + H \rightarrow CD_3 + HD$ on the ZBB3 PES, dimension reduction seems to decrease the reactivity, while keeping the details of the dynamics unchanged.

Conclusions

The performance of the reduced-dimensionality quasi–classical trajectory method corresponding to the Palma-Clary model was assessed in comparison with full-dimensional QCT calculations for two isotopologues of the H atom + methane (CD_4 and CD_3H) abstraction reaction. The shape and even the magnitude of the RDQCT excitation functions agree very well with those from FDQCT calculations on the EG-2002 PES for both isotopologues. The agreement is also good on the EG-2009 and ZBB3 PESs for the CD_3H+H isotopic variant. For the CD_4 + H isotope combination, however, the FDQCT and RDQCT cross sections strongly deviate, especially at relatively high collision energies.

Detailed dynamical properties such as opacity functions and product angular distributions were investigated at a collision energy of $50mE_h$. The FD curves were reproduced very well by the RD method for the EG-2002 and EG-2009 PESs, whereas on the most accurate of the potential energy surfaces, ZBB3, the agreement is retained for reaction of CD_3H but not for the reaction of CD_4. For the latter, significant deviation is observed for all studied dynamical characteristics. These results indicate that the goodness of the Palma-Clary model depends on both the nature of the potential energy surface and on the mass combination of the reactants. We can conclude that the applicability of the reduced-dimensionality approximation cannot be taken for granted and it needs to be tested in each specific case.

It is worth mentioning that even when the RD cross sections agree with the FD ones, the rate coefficients calculated from them will probably differ, because the frozen degrees of freedom will have to be taken into account, for example, using Transition State Theory.

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Acknowledgements

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